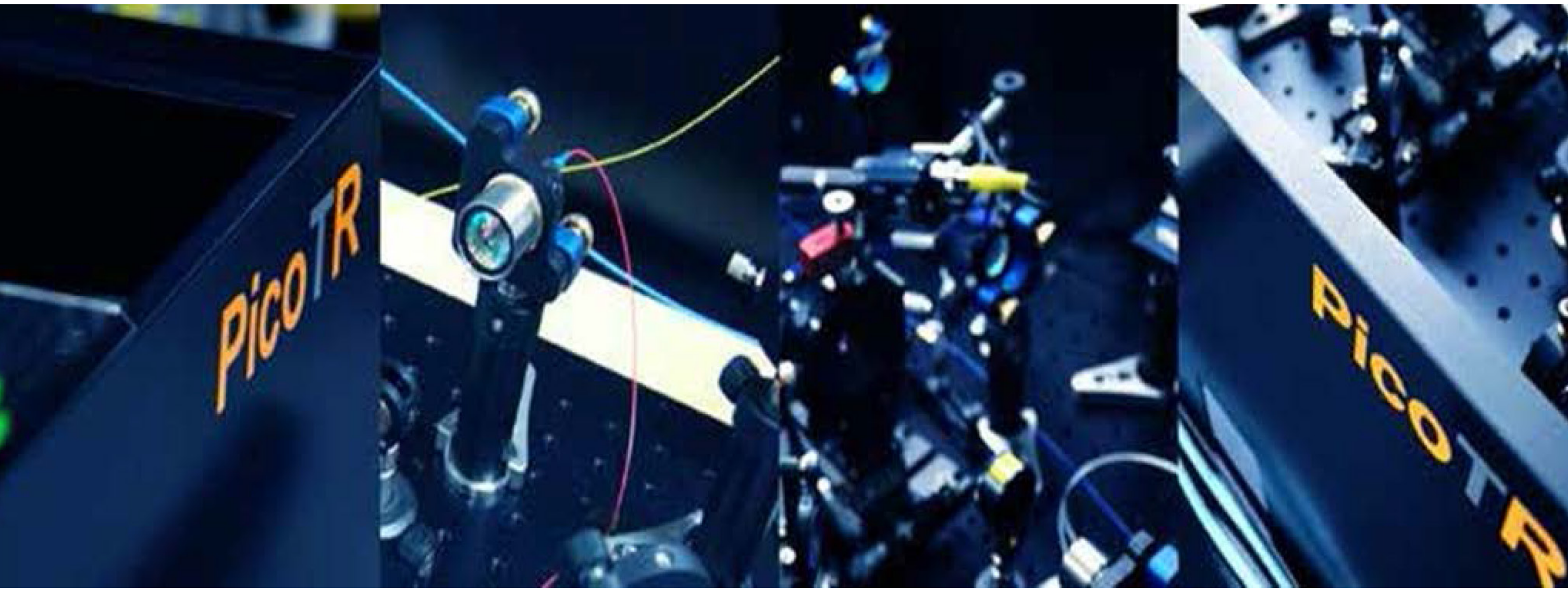
NETZSCH

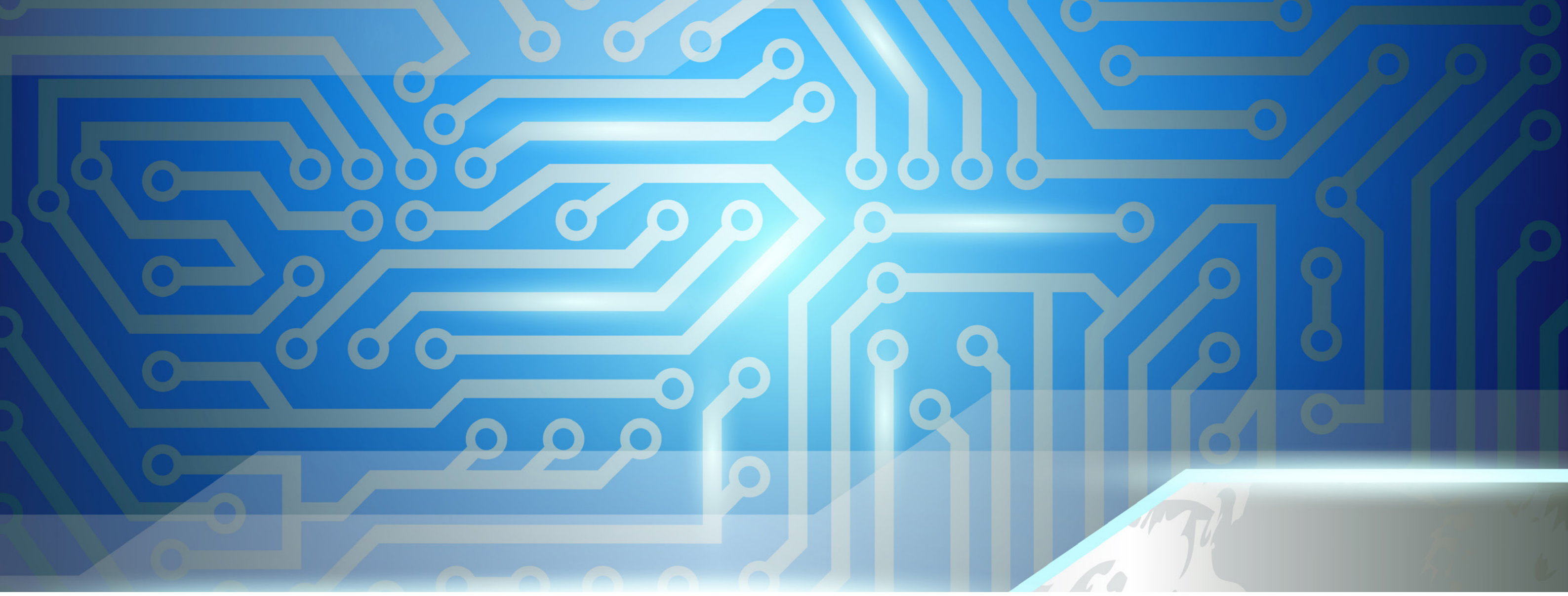


Thermoreflectance by Pulsed Light Heating *NanoTR/PicoTR*

Thermophysical Analysis of Thin Films: Thermal Diffusivity, Thermal Effusivity, Thermal Conductivity and Interlayer Thermal Resistance

PicoTherm from the National Institute of Advanced Industrial Science and Technology (AIST)

Leading Thermal Analysis ■



Thermoreflectance –
The Laser Flash Method for Thin Films

LASER FLASH METHOD –

The Most Established Method for the Determination of Thermal Diffusivity

In modern industries, the knowledge of thermal properties, specifically thermophysical properties, becomes more and more important. They are required, for example, for the development of heat release materials of advanced and miniaturized electronics, thermoelectric materials as sustainable energy, insulating materials for saving energy, TBCs (thermal barrier coatings) for turbine blades, and safety operation of nuclear plants, etc.

Among the thermophysical properties, the thermal conductivity is of paramount importance. The determination of the thermal diffusivity/thermal conductivity can be realized with the established laser flash method (LFA). This method has been known for many years to provide reliable and accurate results. Sample thicknesses typically range from 50 µm to 10 mm.

NETZSCH is a world-wide leading manufacturer of instruments for testing thermophysical properties, specifically of laser flash analyzers. These LFA systems are used in the fields of ceramics, metals, polymers, nuclear research, etc.

THERMOREFLECTANCE –

The Method for the Determination of Thermal Diffusivity in the Thickness Range of Nanometer

PicoTherm

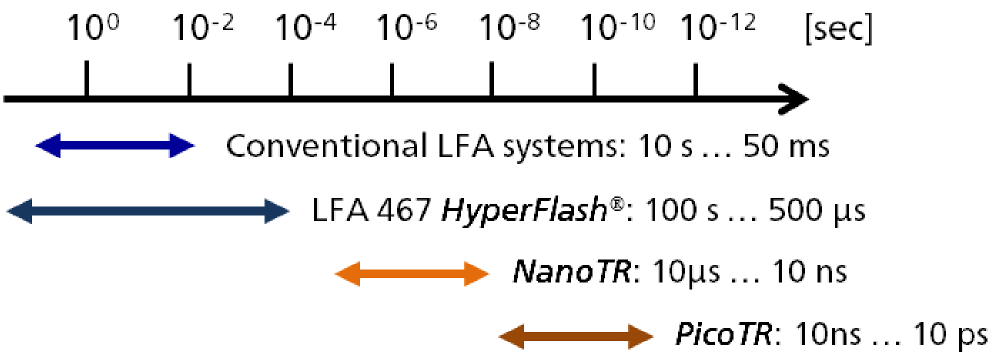
With the significant progress in the design of electronic devices and the associated need for an efficient thermal management, accurate thermal diffusivity / thermal conductivity measurements in the nanometer range are more than ever crucial. Materials with such thicknesses are used in phase-change memories (PCM), thermoelectric thin films, light emitting diodes (LED), interlayer dielectrics, and transparent conductive films (FPD), etc.

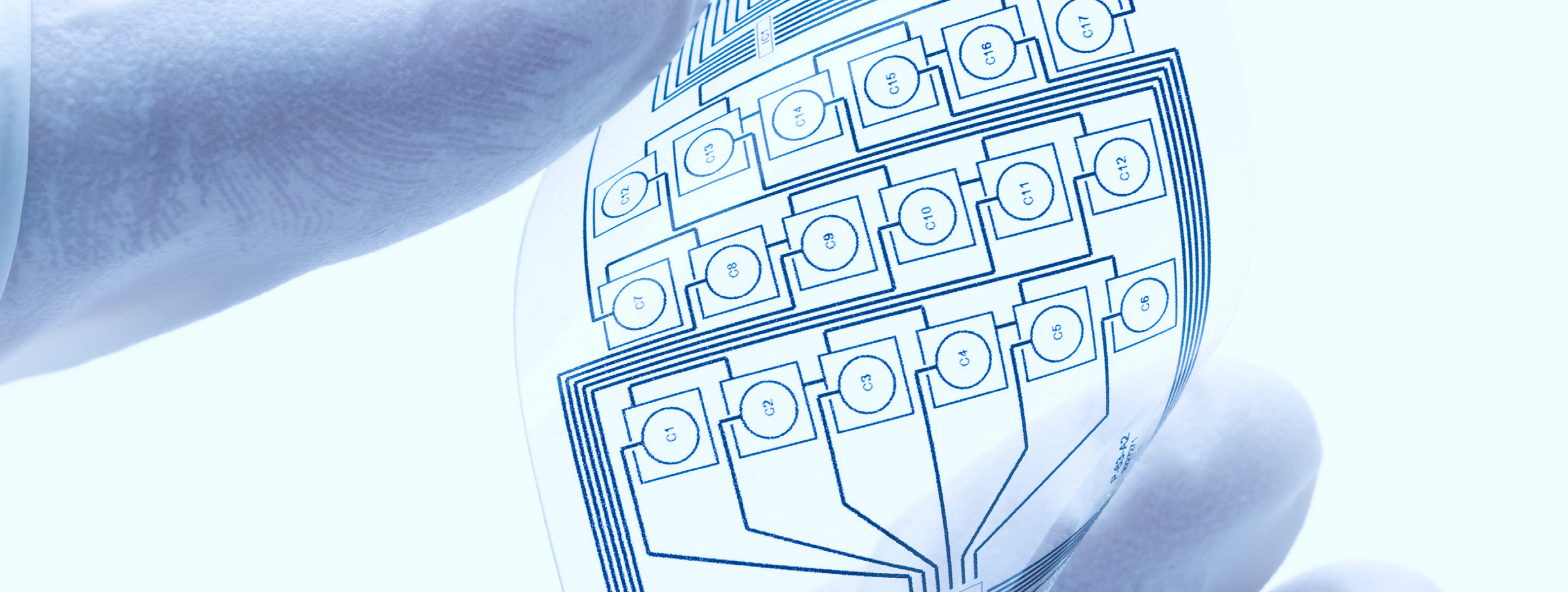
The National Institute of Advanced Industrial Science and Technology (AIST), Japan, already responded to industrial requirements with the development of a "pulsed light heating thermoreflectance method" in the early 90's, which allowed for absolute measurements of the thermal diffusivity of thin films. As an AIST start-up **PicoTherm** Corporation was established in 2008 with the launch of a nano-second thermoreflectance apparatus *"NanoTR"* and a pico-second thermoreflectance apparatus *"PicoTR"*. These instruments allow for measurements on materials in a thickness range of several 10 µm down into the nanometer range.

In 2014, NETZSCH Japan K.K, a subsidiary of NETZSCH business unit Analyzing &Testing, became the exclusive representative of the **PicoTherm** Corporation. In combination with our LFA systems, NETZSCH can now offer the solution for thin films in the nanometer range up to bulk materials in the range of mm.

Possible Heat Diffusion Times

Thermal Diffusion Time $\tau = \frac{d^2}{a}$





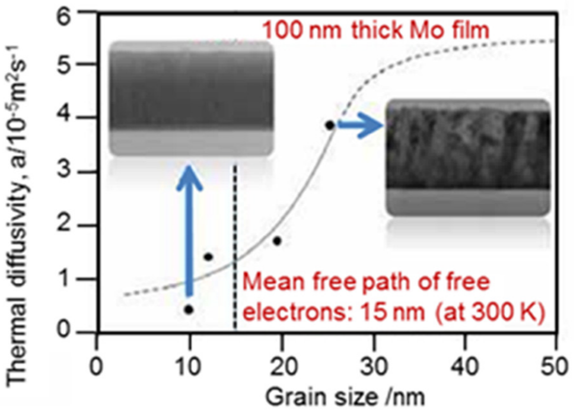
Why Measuring Thin Films?

Thermal Properties of Thin Films are Different from that of Bulk Materials

The thicknesses of nanometer-thin films are often less than the typical grain size. Consequently, their thermophysical properties differ significantly from the bulk material.

The plot below indicates the dependency of thermal diffusivity on the grain size. At decreasing grain size (film thickness), the values for thermal diffusivity decrease, especially close to the mean free path of electrons (~$1.5 \cdot 10^{-5}$ m^2/s at 15 nm). The thermal diffusivity of bulk material is ~$5.4 \cdot 10^{-5}$ m^2/s and therefore three to four times higher.

For this reason, it is essential to carry out the determination of the thermal diffusivity on thin films as well.



Thermal diffusivity of a molybdenum (Mo) thin film compared to bulk material; Japanese Journal of Applied Physics 48 (2009) O5ECO1 Furnished by AIST

What is Thermoreflectance?

Thermoreflectance Measures the Change in Reflected Light Due to a Change in Temperature

The thermoreflectance technique makes use of the material's temperature dependent reflectivity. By measuring the reflected energy of a constant laser probe, the surface temperature fluctuations can be accurately monitored. Thermoreflectance usually performs much faster than the conventional radiation-sensing IR detector.

$$\Delta T = \left[\frac{1\,\partial}{R\,\partial}\right]^{-1} \frac{\Delta R}{\Delta T}$$

where

ΔT	change in temperature
R	reflectivity
Δ	change in reflectivity

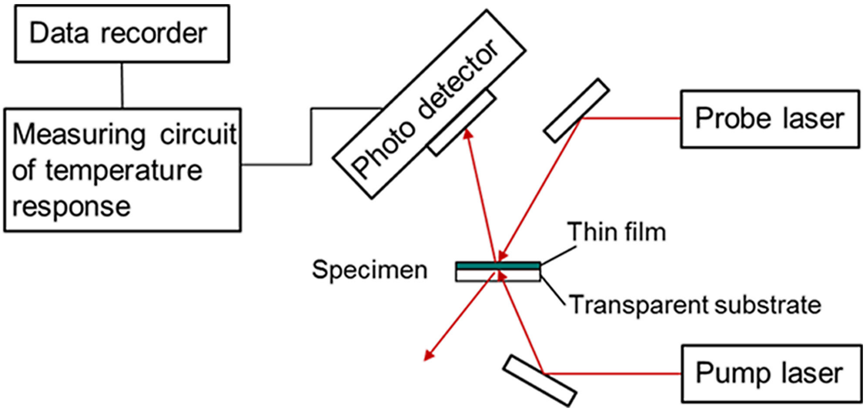
Application Range

- Thermoelectric material, solar cell, fuel cell, OLED
- Semiconductor memory, storage, metals, FeRAM, MRAM, PRAM, LSI, power devices, phase change and magnetic recording film, diffusion barrier film
- LED, ceramic composites, electronics, resins for insulation films, transparent conductive films for FPD, interlayer dielectrics, gate insulators

Measurement Principle

The front surface of a thin film on a transparent substrate is heated by a pulsed laser source for heating (pump laser). At the same time, the front or rear surface of the thin film is irradiated by a laser source for temperature monitoring (probe laser).

Combined with the photo detector, the reflectivity can be evaluated as a function of time, and the curve of the temperature rise can be obtained. By fitting the mathematical model to the history curve of the temperature, the thermal diffusivity can be determined.



Measurement setup

Thermoreflectance Methods

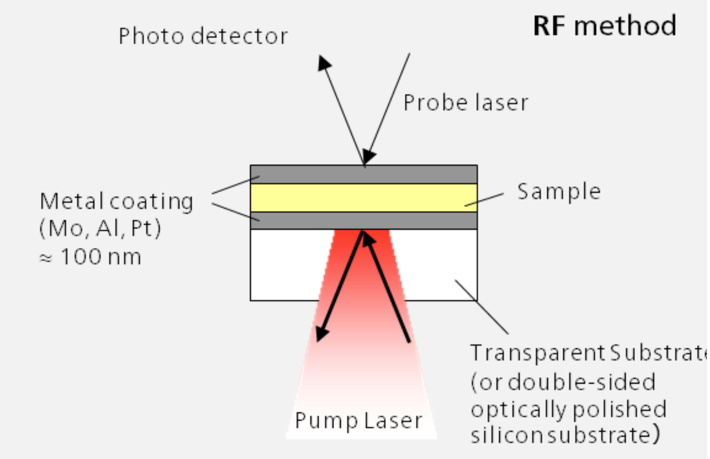
ULTRAFAST LASER FLASH METHOD – REAR HEATING/FRONT DETECTION (RF)

Determination of Thermal Diffusivity and Interfacial Thermal Resistance

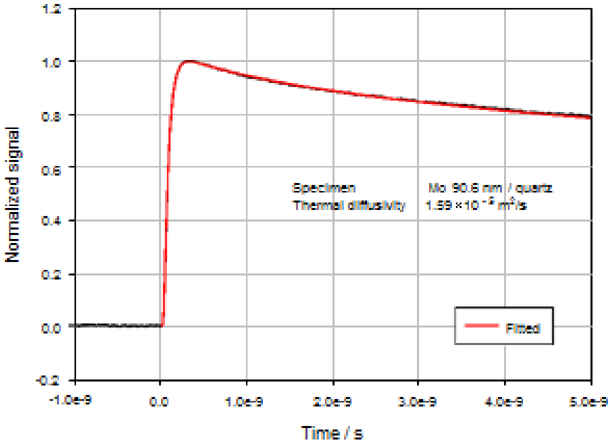
The fact that the thermophysical properties of thin layers and films differ considerably from those of the corresponding bulk material requires a technique which overcomes the limitations of the classical laser flash method (LFA). This so-called ultrafast laser flash technique is also known as the rear heating/front detection method.

The measurement setup is similar to the conventional LFA: detector and laser are on opposite sides of the sample which is located on a transparent substrate. The measured thermal diffusivity is the component through the thickness perpendicular to the sample's surface. The pump laser irradiates the sample's rear side (upper picture).

As the sample heats up, its surface thermoreflectance varies. The thermal diffusivity is calculated from the temperature rise (lower plot). Here, the thermal diffusivity of a thin metal film (Mo) was determined to $1.59 \cdot 10^{-5}$ m²/s.



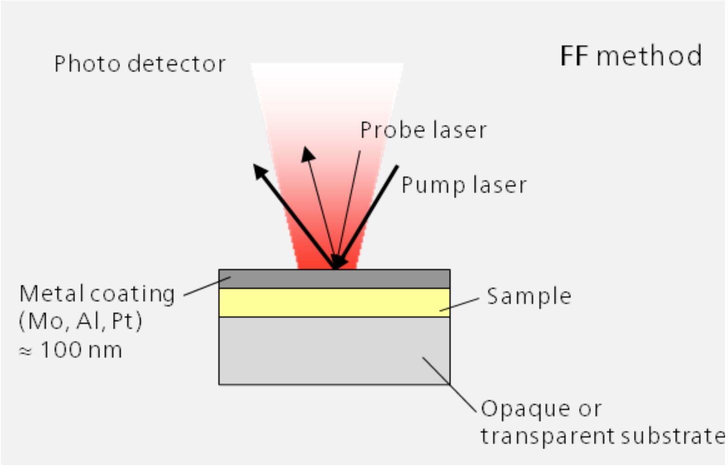
RF configuration specifically for transparent substances



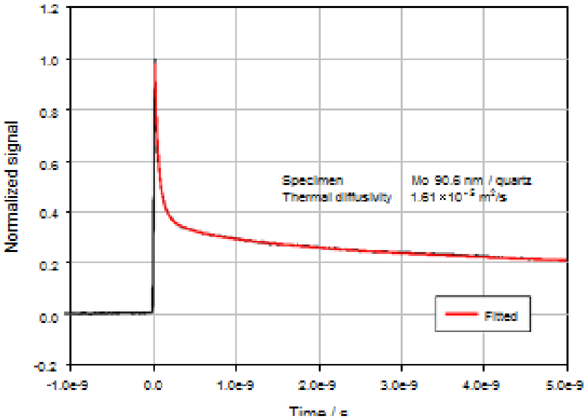
Temperature history curve and measured thermal diffusivity of Mo thin film (90 nm) with RF method

TIME DOMAIN THERMOREFLECTANCE – FRONT HEATING/FRONT DETECTION (FF)

Determination of Thermal Diffusivity and Thermal Effusivity



FF configuration specifically for opaque substrates



Temperature history curve and measured thermal diffusivity of Mo thin film (90 nm) with FF method

In addition to the RF method, measurements can also be made in a front heating/front detection (FF) configuration. The term "front" refers to the open surface of the thin film deposited on a substrate, while "rear" refers to the boundary between the thin film and the substrate.

In the FF measurement setup (upper picture), the detector and laser are on the same side of the sample. An area of the front face of the thin film with a diameter of several tens of micrometers is heated by a pump laser, and a probe laser points at the same position. The change in the surface temperature is observed.

This method can be applied to thin layers on non-transparent substrates for which the RF technique is not suitable.

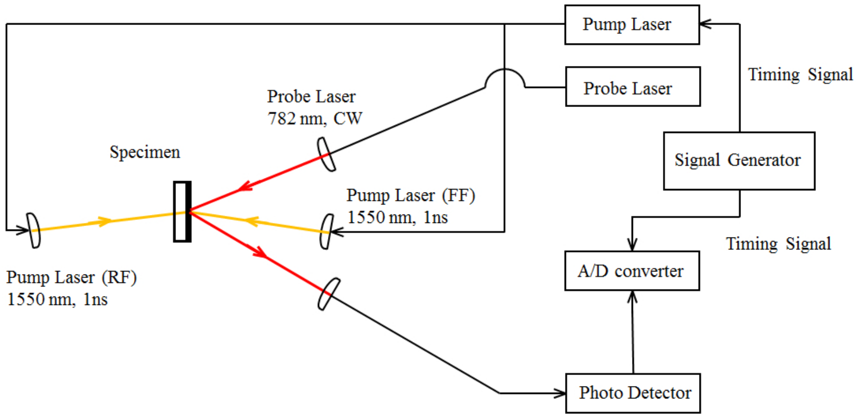
In the example on the left, the thermal diffusivity of a thin metal film (Mo) was determined to 1.61 $\cdot 10^{-5}$ m^2/s by applying the FF method. The results prove the high agreement between RF and FF modes (deviation < 2%).

NanoTR

Principle of *NanoTR*

NanoTR's state-of-the-art signal processing technology allows high speed measurements. With this thermoreflectance apparatus, a laser pulse of 1 ns pulse width is periodically (20 µs) irradiated to the sample. The resulting temperature response is applied to a CW laser (probe laser). Excellent s/n ratio can be attained by high speed integration of repetitive signals. It can be easily switched between the RF and FF configurations though the software for a wide variety of samples.

NanoTR is in accordance with JIS R 1689, JIS R 1690, and SI traceable by the thin film standard of heat diffusion time (RM1301-a), supplied from AIST.

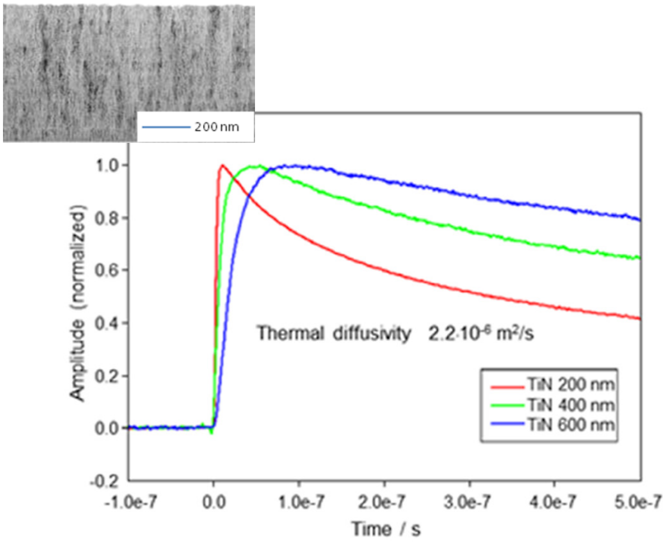


Instrument setup of the *NanoTR* apparatus

Applications

Temperature History Curve of TiN Thin Films Consisting of Different Thicknesses

This plot shows temperature excursions of TiN thin films 200, 400, and 600 nm thick, measured in the RF configuration. The front surface of the thin films was heated by laser pulses, and the resultant temperature rise of the back surface was monitored.

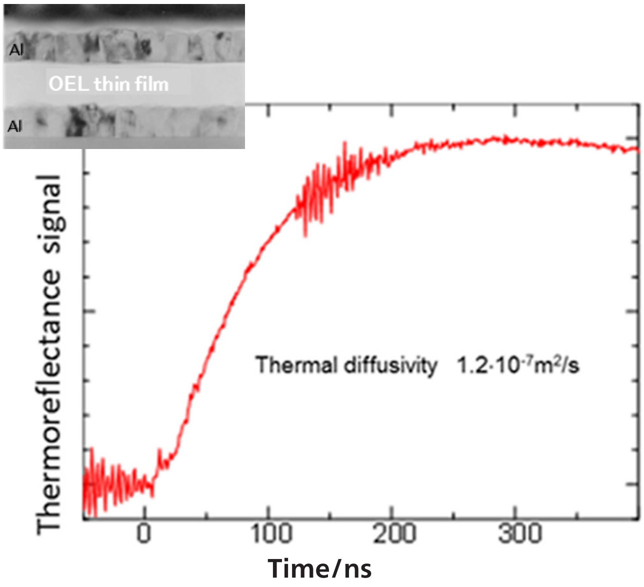


Thermoreflectance signals of TiN films obtained by rear heating/front detection configuration (RF)

Temperature History Curve of an OEL Thin Film Betwen Two Metal Layers

This plot shows the temperature history curve of an OEL thin film, measured in the RF configuration. Since the OEL thin film is transparent to the wave length range of the pump and probe laser, Al thin layers were deposited on both sides of OEL layer.

A three-layer analysis was applied to the temperature curve, resulting in a calculated thermal diffusivity value of the OEL layer of $1.2 \cdot 10^{-7}$ m²/s.



Thermoreflectance signals of an OEL thin film obtained by rear heating/front detection configuration (RF)

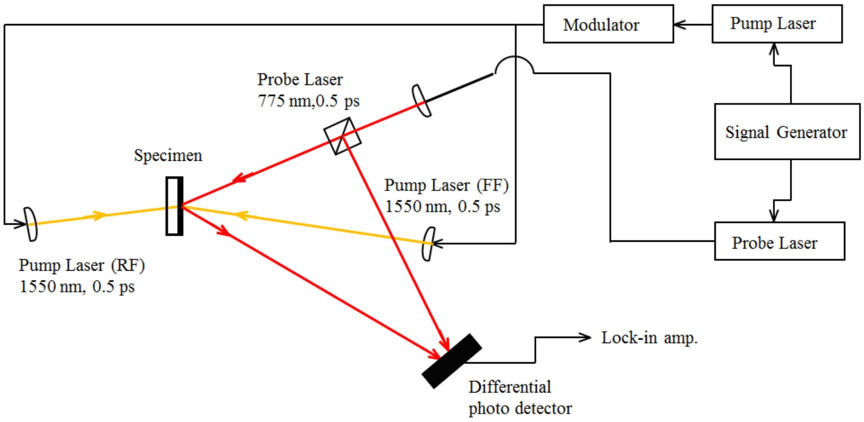
PicoTR

Principle of *PicoTR*

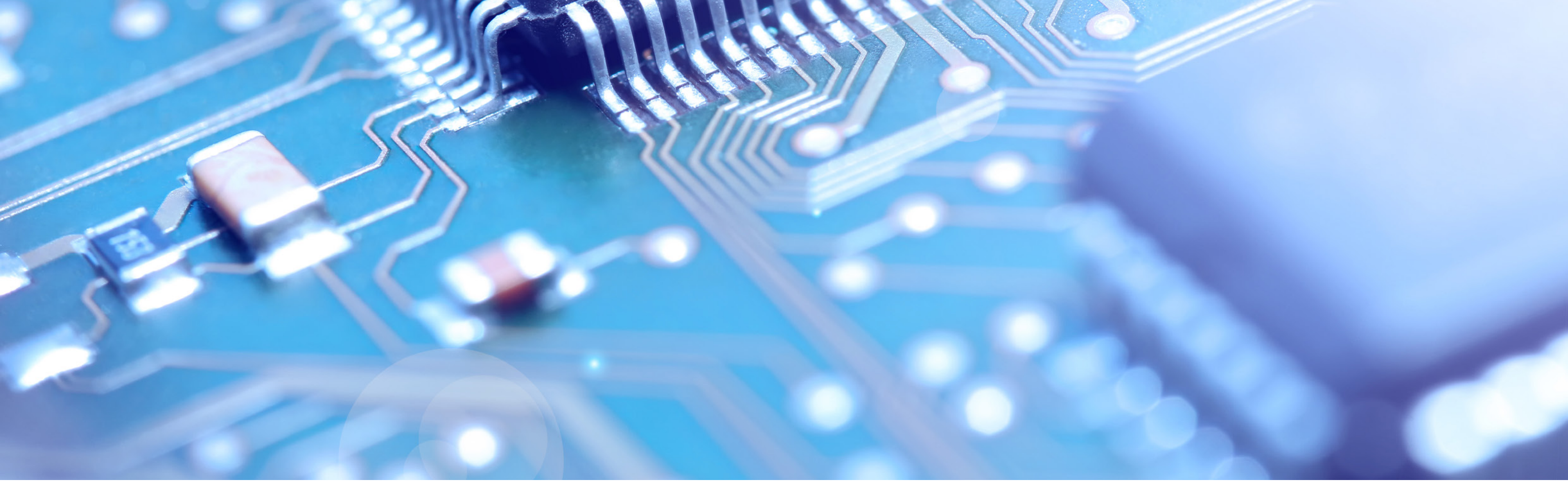
With picosecond thermoreflectance analyzer *PicoTR*, laser pulses (pump laser) of 0.5 ps pulse width are applied to the sample with the time period of 50 ns. The temperature response is detected with the probe laser.

PicoTR allows for an easy switching between the RF and FF mode by the user.

PicoTR is in accordance with JIS R 1689, JIS R 1690.



Instrument setup of the *PicoTR* apparatus



Applications

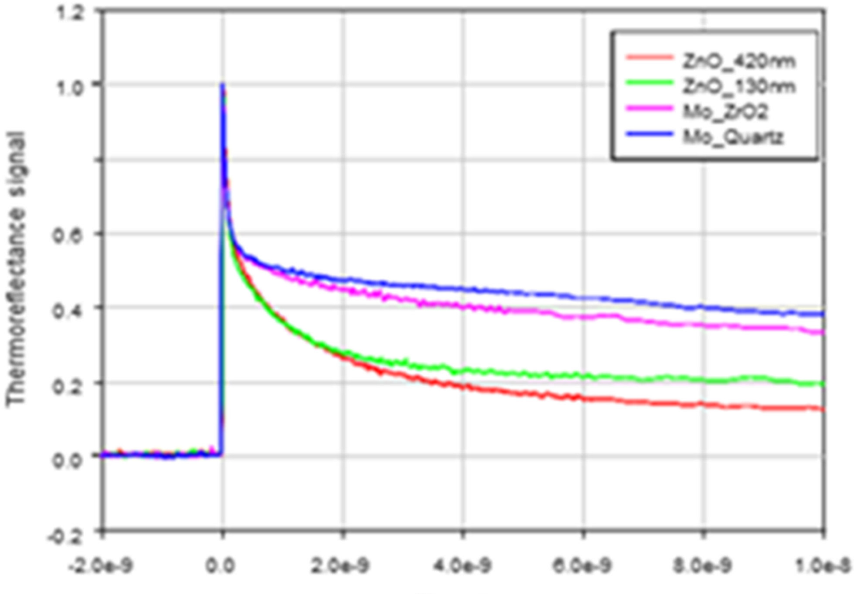
Temperature History Curve of ZnO Thin Film on a Transparent Substrate

Due to its wide band gap and large exciton-binding energy, ZnO has been attractive for applications in optoelectronic devices, ultra-violet emitters, sensors, etc.

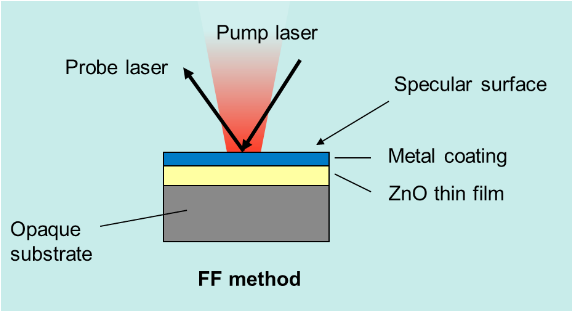
The plot shows temperature history curves of translucent ZnO thin films coated by deposited Mo layers on their surface. Sharp peaks are observed immediately after the irradiation of the pump laser beam. With increasing time, the decrease of the surface temperature can be monitored due to heat diffusion into the Mo layer. After approximately 1 ns, the heat wave reaches the boundary and starts diffusing into the ZnO layer. The thermal effusivity* (also known as the heat penetration coefficient) is determined to 8570 J/($m^2 \cdot s^{0.5}$ K).

As expected, this example demonstrates that the cooling rate of the surface temperature is influenced by the thermal effusivity of 2nd layer.

We kindly thank the National Institute for Material Science (NIM) for the measurements.



PicoTR measurements on ZnO samples in FF configuration (see picture below): 100 nm Mo on ZnO 420 nm (red); 100 nm Mo on ZnO 130 nm (light green); 100 nm Mo on ZrO_2 (purple); 100 nm Mo on Quartz (blue)



*The thermal effusivity of a material is the square root of the product of the thermal conductivity, density and heat capacity. It is a measure of the material's ability to exchange thermal energy with its surroundings.

PicoTR – Applications

Temperature History curve of SiO_2 Thin films

The upper plot shows the temperature history curves of SiO_2 thin films with different thicknesses, measured with *PicoTR* in the RF configuration.

Mo thin layers were deposited on the both sides of the SiO_2 thin films, and triple layer analysis was applied.

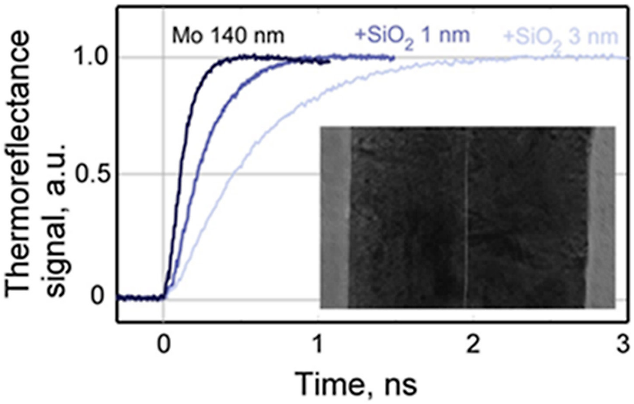
For each of the curves obtained with the different layers of SiO_2, the areal heat diffusion time* was calculated and plotted as a function of the thickness.

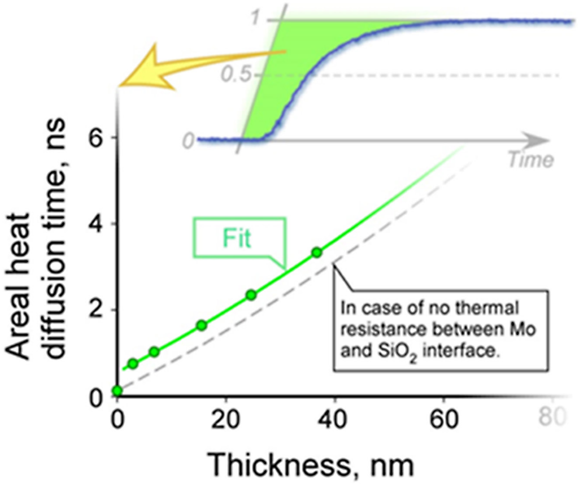
Based on these results, the thermal resistance of the SiO_2/Mo interface and the thermal diffusivity (a) of SiO_2 layer can be calculated to $8.8 \cdot 10^{-7} m^2/s$ using the formula:

$$\partial = \left(\frac{Thickness^{2}}{\sigma \cdot Areal\ Heat\ Diffusion\ Time}\right)$$

The interfacial thermal resistance can be determined to $2 \cdot 10^{-9} m^2 \cdot K/W$.

The principle of the three-layer analysis can be seen in Jpn.Appl. Phys. 50(2011) 11RA01.





*Thickness dependence of the areal diffusion time of So_2: The areal heat diffusion time is defined as the integral of the rising segment of the normalized temperature response curve over the thermoreflectance axis.

Traceability to National Standard

NanoTR and *PicoTR* allow for an absolute measurement of the thermal diffusivity in the case of an opaque sample and a transparent substrate. For all other cases such as opaque substrate and transparent thin film, reference materials are available made of Molybdenum (CRM 5808-a, for PicoTR) and TiN (RM 1301-a, for NanoTR). It is supplied by AIST, the Japanese National Institute of Advanced Industrial Science and Technology. This guarantees the traceability to national standard.
NanoTR and *PicoTR* are calibrated to ensure traceability to Japanese standards. The instruments are in accordance with the Japanese Industrial Standards (JIS):

- JIS R 1689 "Determination of thermal diffusivity of fine ceramic films by pulsed light heating thermoreflectance method"
- JIS R 1690 "Determination of interfacial thermal resistance between fine ceramic film and metal film"

Technical Specification

		NanoTR	*PicoTR*
Pump Laser	Pulse width	1 ns	0.5 ps
	Wave length	1550 nm	1550 nm
	Beam diameter	100 µm	45 µm
Probe Laser	Pulse width	contiuous	0.5 ps
	Wave length	785 nm	775 nm
	Beam diameter	50 µm	25 µm
Measurement items		Thermal diffusivity and effusivity, interfacial resistance	
Measureument time		Less than 30 seconds	Less than 5 minutes
Sample film thickness (RF method)	Resin	30 nm ... 2 µm	10 nm ... 100 nm
	Ceramics	300 nm ... 5 µm	10 nm ... 300 nm
	Metal	1 µm ... 20 µm	100 nm ... 900 nm
Sample film thickness (FF method)		Thicker than 1 µm	Thicker than 100 nm
Substrate	Material	Opaque/Transparent	
	Size	10 ... 20 mm square	
	Thickness	1 mm or less	
Thermal diffusivity	Range	0.01 ... 1000 mm^2/s	
	Accuracy	±6.2% (for CRM 5808A in RF mode, 400 nm thickness Mo)	
	Repeatability	±5%	
Software		Calculation of thermal properties, multilayer analysis, database	
Power supply		AC100 V ~240 V (±10%); 50/60 Hz, 0.5 kVA	

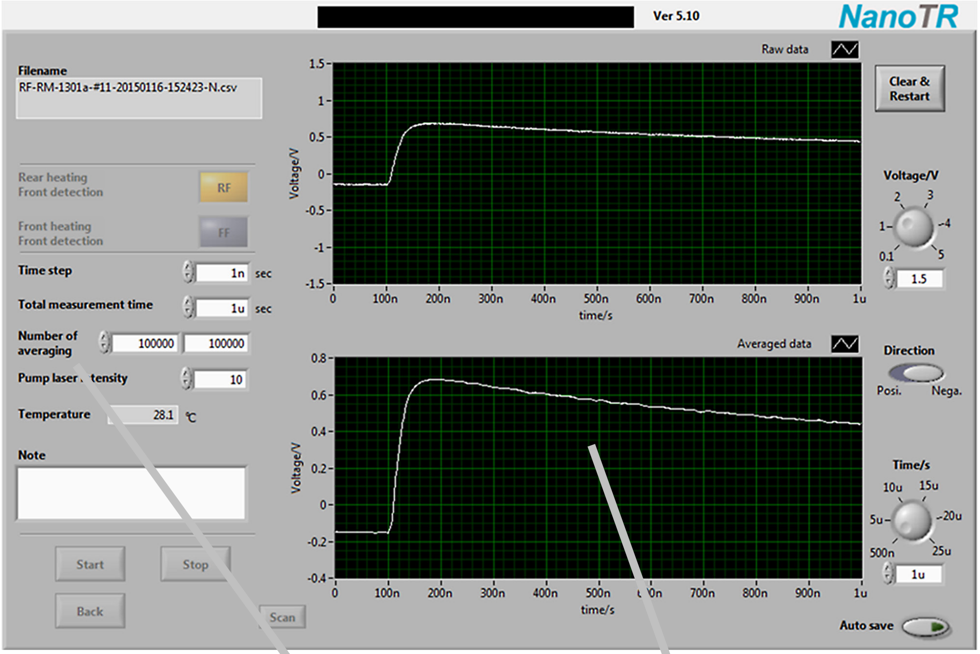
Software

IN-SITU DISPLAY AND ANALYZING

100,000 SHOTS

The state-of-the-art measurement/analysis software of *NanoTR/PicoTR* has an easy-to-handle user interface which allows for a precise determination of the thermal properties of thin films. The laser beam focusing can be adjusted by the software and CCD picture can be obtained.

NanoTR/PicoTR software runs under Microsoft Windows.



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Ver 5.10

Filename: RF-RM-1301a-#11-20150116-152423-N.csv

Time step: 1n sec

Total measurement time: 1u sec

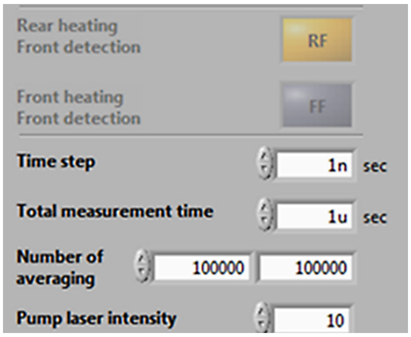
Number of averaging: 100000 100000

Pump laser intensity: 10

Temperature: 28.1 ℃

Voltage/V: 1.5

Time/s: 1u



Time step: 1n sec

Total measurement time: 1u sec

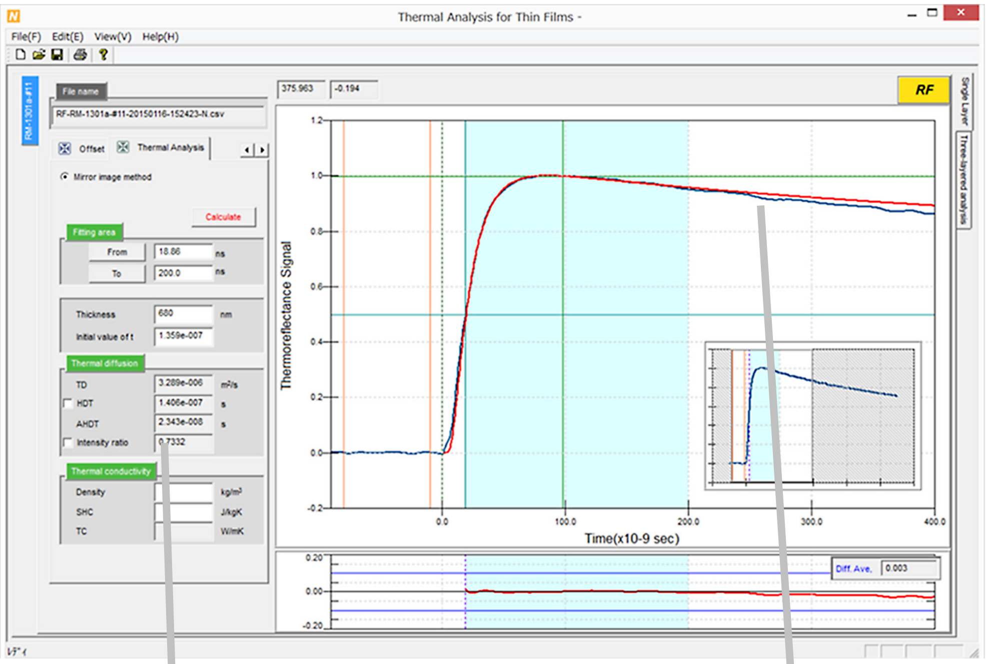
Number of averaging: 100000 100000

Pump laser intensity: 10

Measurement

- Choose point distance: 1 ns
- Measurement time (duration): 1 µs (for one measurement curve)
- Averaged: Temperature rise on the base of 100,000 single measurements

OBTAINING RESULTS IN SECONDS



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375.963 -0.194

● Mirror image method

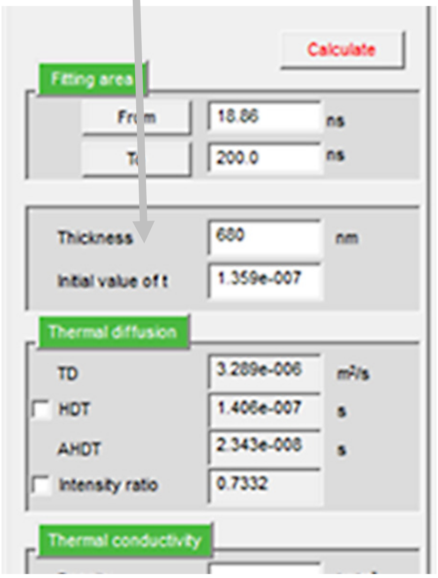
Fitting area
From 18.86 ns
To 200.0 ns

Thickness 680 nm
Initial value of t 1.359e-007

Thermal diffusion
TD 3.289e-006 m²/s
☐ HDT 1.406e-007 s
AHDT 2.343e-008 s
☐ Intensity ratio 0.7332

Thermal conductivity
Density kg/m³
SHC J/kgK
TC W/mK

Diff. Ave. 0.003



Fitting area
From 18.86 ns
To 200.0 ns

Thickness 680 nm
Initial value of t 1.359e-007

Thermal diffusion
TD 3.289e-006 m²/s
☐ HDT 1.406e-007 s
AHDT 2.343e-008 s
☐ Intensity ratio 0.7332

Thermal conductivity

Analysis

- Model fit
- Temperature rise
- Calculated thermal diffusivity; results obtained within a few seconds based on several single measurements

The NETZSCH Group is a mid-sized, family-owned German company engaging in the manufacture of machinery and instrumentation with worldwide production, sales, and service branches.

The three Business Units – Analyzing & Testing, Grinding & Dispersing and Pumps & Systems – provide tailored solutions for highest-level needs. Over 3,300 employees at 210 sales and production centers in 35 countries across the globe guarantee that expert service is never far from our customers.

When it comes to Thermal Analysis, Calorimetry (adiabatic & reaction) and the determination of Thermophysical Properties, NETZSCH has it covered. Our 50 years of applications experience, broad state-of-the-art product line and comprehensive service offerings ensure that our solutions will not only meet your every requirement but also exceed your every expectation.

Leading Thermal Analysis ▪

NETZSCH offers a complete product range for the determination of

- Thermal Diffusivity / Thermal Conductivity
- Seebeck Coefficient / Electrical conductivity
- Specific heat
- Density
- Thermal Effects

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NGB · Thermoreflectance · EN · 200 · 0517 · NWS · Technical specifications are subject to change.